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⑤④ **Imitation cheese products containing modified starches as partial caseinate replacements.**

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**FOOD SCIENCE & TECHNOLOGY**, August 1974,  
abstract no. 74041625 J. DOLEZALEK et al.:  
"Method for the manufacture of dairy products"

⑦③ Proprietor: **National Starch and Chemical Corporation**  
Box 6500  
Bridgewater, N.J. 08807 (US)

⑦② Inventor: Zwiercan, Gary A.  
10 Yewland Drive  
Knutsford Cheshire WA168AP (GB)  
Inventor: Lenchin, Julianne M.  
2433 Old Stone Mill Drive  
Cranbury New Jersey 08512 (US)  
Inventor: Lacourse, Norman L.  
57-02 Hunters Glen Drive  
Plainsboro New Jersey 08536 (US)

⑦④ Representative: Hagemann, Heinrich, Dr. et al  
Patentanwälte GEYER, HAGEMANN &  
PARTNER Postfach 860329  
D-8000 München 86 (DE)

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**HANDBOOK OF WATER SOLUBLE GMBH AND RESINS (1980) ROBERT L. DAVIDSON**  
**CHAPTER 22 STARCH AND ITS MODIFICATION**  
- PP 22-27.

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## Description

This invention relates to the partial replacement of the caseinates present in imitation cheese products, such as cheddar, processed American and especially mozzarella, by selected edible modified starches.

5 Early attempts to reduce cheese costs led to the development of cheese analogs in which vegetable fat replaced the more costly milk fat. Such analogs were usually manufactured by traditional methods from skim milk containing dispersed vegetable fats and were generally referred to as "filled" cheeses.

Later economic incentives and technical advances led to the development of fabricated cheese analogs manufactured fundamentally from casein or its derivatives, vegetable fats or oils, salts, acids, and  
10 flavorings. Since casein derivatives are legally defined as nondairy ingredients, the fabricated analogs were referred to as "imitation" cheeses.

Imitation cheese products include very high-moisture content cheeses such as cream cheese; high moisture content cheeses such as blue cheese and mozzarella, the latter accounting for a major portion of the casein-based imitation cheese market; medium-moisture cheeses, such as cheddar and provolone;  
15 low-moisture cheeses, such as romano and parmesan; and pasteurized processed cheeses such as American cheese, cheese spreads and cheese products. These imitation cheese products provide the flavor and functionality of natural cheese at a reduced cost and, in addition, are lower both in calories and cholesterol since the animal fat has been replaced by vegetable fat.

Sodium, potassium, and calcium caseinates, as well as those salts generated *in situ* by treating acid  
20 casein and rennet casein with the appropriate alkali, are used in the preparation of imitation cheese products. Besides providing a major protein source, the caseinates, alone or in combination, possess unique setting, textural and emulsification properties that make them ideal, and their moderately low viscosity permits their use at high solids.

The world supply of casein and caseinates, however, appears to have reached its maximum output.  
25 The current high cost and uncertain future availability have become a major concern to food processors. For these reasons, the processors have been trying to find a readily available caseinate substitute, preferably a low cost substitute, to partially or totally replace the caseinates in imitation cheese products. Some attempts have been made to utilize dry vegetable protein isolates (e.g. soy isolates) as replacements. The isolates lack the functionality of the caseinates and have generally only been useful as extenders. The  
30 isolates have to be specially treated to provide cheeses with sufficient melt (see US—A—4,349,576 and even then severe shearing during the cheese preparation will substantially reduce the melt value. A recent article in Food Processing (October 1981, pp. 28—29) discloses that a protein mixture (25% casein, 25% soy flour, 25% wheat gluten, and 25% alfalfa protein) is being used with some success in imitation mozzarella cheese; however, the final product does not provide "all desirable characteristics, including flavor".

35 Thus, there is still a need for a readily available caseinate replacement which will provide the gelling and emulsion-stabilizing properties required during the cheese preparation and which will still provide cheese products having a desirable flavor and textural properties (i.e. especially gel, melt, and shredding and slicing characteristics) comparable to the caseinate-based imitation cheeses.

Flours and starches have been used in various cheese products as thickeners and/or binders as well as  
40 to improve specific properties. They have not, however, been used as caseinate replacements to provide the properties typically supplied by the caseinates.

In natural cheese products, for example, cyclodextrin has been added to increase moisture retention and storage life (Jap. Kokai Tokyo Koho 81 75,060); phosphorylated starch (about 2%) has been used as a thickener in blends of Cheshire and Emmenthal cheese to provide a non-stringy product (FR—B—  
45 1,570,860); aqueous corn starch mixtures (in place of the previously used milk or butter) have been blended with melted ripe cheese to give a stable soft food product having the consistency of butter (FR—B—1,566,665); starches have been used in processed cheese products prepared from natural cheese, milk powder and other ingredients (Food Engineering, November 1980, p. 25); and pregelatinized corn, potato and tapioca starches have been used as stabilizers (against the deleterious influences of freezing  
50 and thawing) in cheese cake and cheese pie fillings (US—A—3,666,493). In addition, potato starch (3—6%) has been used in admixture with a heated whey solution (65°C) as a coating to improve the general appearance of hard cheeses (Pol. 54,548).

In cheese analogs and simulated cheese products, for example, corn starch hydrolysates (e.g. corn syrup) have been used to bind the water and prevent or retard its loss, as well as to add gloss, palatability,  
55 and body texture, to cheese foods based on vegetable oils, animal or vegetable proteins, and emulsifying metal salts US—A—3,310,406; ungelatinized flours (e.g. 3% tapioca flour) have been added, as optional ingredients (0—5%), to a caseinate-containing cheese substitute to aid in the firmness of the cheese substitutes resembling pasta filata or cheddar cheese (AT—B—335,830; DE—A—2,411,945; US—A—  
60 3,922,374; and US—A—4,104,413); flour and hydrogenated vegetable oils have been used as the matrix in intermediate moisture (about 12%), high flavor-impact cheese analogs containing dehydrated cheese and artificial flavorings which are prepared by homogeneously mixing the components at low temperature and extruding the mass to form rods which are further processed into cubes, strips or grated particles (Food Product Development, June 1980, pp. 42—43); gelatinized high amylose starches and their derivatives have been used as binders for various edible protein pieces in integral simulated cheese products containing no  
65 fat (3,836,677); and pregelatinized starches (e.g. corn, wheat, waxy maize and tapioca) have been used in

shelf-stable, high protein extruded cheese products prepared from a mixture of cheese, starch, high protein binding agent, water, sugar or sugar equivalents and optionally 1—7% of an edible oil (US—A—3,741,774).

Thus, there is a need for edible modified starches with gelling and emulsion-stabilizing properties for use as partial caseinate replacements in imitation cheeses, especially mozzarella cheese.

5 The present invention provides an imitation cheese product containing at least one edible caseinate characterized in that up to about 80% by weight of the caseinate is replaced by an edible modified starch; the starch being a pregelatinized converted starch having a water fluidity (WF) of 5—90 and an amylose content of at least 15% and less than 40%, or the derivatives thereof prepared by treatment with up to about 10% propylene oxide, up to about 2.0% succinic anhydride, up to about 3.0% octenylsuccinic  
10 anhydride, or with a sufficient amount of acetic anhydride to provide a maximum of about 2.5% bound acetyl, or with a sufficient amount of a sodium or potassium orthophosphate, sodium or potassium tripolyphosphate, or mixtures thereof to provide a maximum of about 0.4% bound phosphate, or the moderately crosslinked products thereof prepared by treatment with phosphorus oxychloride, epichlorohydrin, sodium trimetaphosphate, or adipic-acetic anhydride, or the derivatized, moderately  
15 crosslinked starches; the converted starches being selected from the fluidity starches prepared by treatment with acid or enzyme and oxidized starches prepared by treatment with up to about 2% active chlorine; the treatment percentages being by weight based on the starch; whereby the starch-caseinate cheese product is functionally equivalent to the caseinate-based imitation cheese product.

In a preferred embodiment, it provides an imitation cheese product functionally equivalent to a  
20 caseinate-based imitation cheese product selected from the group consisting of mozzarella cheese, cheddar cheese, and processed American cheese, which comprises water, an edible vegetable fat or vegetable oil, cheese additives, and a mixture of 20—80% by weight of sodium and calcium caseinate and 80—20% by weight of the edible modified starches discussed hereinabove, preferably those having an amylose content of 20—30% and water fluidity of 20—80.

25 In the most preferred embodiment, it provides an imitation mozzarella cheese product equivalent or substantially equivalent in shred, melt, and string, wherein the starch is a 20—80 WF corn starch derivative prepared by treatment with 1—3% octenylsuccinic anhydride, 0.25—2% propylene oxide, or with a sufficient amount of acetic anhydride (typically 0.25—3%) to provide 0.13—1.6% bound acetyl or a 40—80  
30 WF oxidized potato starch prepared by treatment with 0.5—1.5% active chlorine, the starch being present in an amount of 25—50%. The most preferred starch derivative is a 35—50 WF corn starch derivative prepared by treatment with 1—2% octenylsuccinic anhydride or a 65—70 WF crosslinked corn starch derivative prepared by treatment with up to 0.01% phosphorus oxychloride and 1—2% octenylsuccinic anhydride.

35 It also provides a method for preparing an imitation cheese product from water, a melted vegetable fat or a vegetable oil, an edible caseinate and cheese additives by adding thereto, as a replacement for up to 80% by weight of the caseinate, an edible modified starch, the water and melted fat or oil being gelled and emulsion-stabilized by the caseinate-starch mixture, the starch being selected from the group of edible modified starches discussed hereinabove.

40 As used herein, the term "imitation cheese" is intended to refer to any cheese analog typically prepared from water, vegetable fats or vegetable oils, caseinates, the edible modified starches described herein, and other typical cheese additives such as natural and/or artificial flavorings, salts (sodium chloride and other salts), acids, colors, emulsifiers, stabilizers, preservatives and optionally other proteins such as vegetable proteins.

45 The applicable starch bases which may be used in preparing the pregelatinized, converted starches for use herein as partial caseinate replacements may be derived from any plant source other than waxy starches or high amylose starches having an amylose content of 40% or above. Suitable starches should have an amylose content of at least 15% and less than 40%, preferably 20—30%, by weight. These include starches such as corn, potato, sweet potato, wheat, rice, sago, tapioca and sorghum having amylose  
50 contents of up to about 30% and starches such as smooth pea, Canadian pea, cocoa bean, and winged bean having amylose contents up to about 40%. Waxy starches such as amioca which contain little or no amylose may be blended with the above amylose-containing starches to provide a useful blend having an amylose content at or above the minimum value.

55 The starch bases must be converted and pregelatinized to be suitable for use herein. Conversion degrades the starch and reduces the viscosity of the cooked starch dispersions. Slightly stabilized converted starches are preferred, such as the derivatized fluidity starches and the oxidized starches. Stabilization improves the melt of the final cheese product.

Suitable converted starches include acid—or enzyme—converted starches (often referred to as fluidity starches) and oxidized starches (often referred to as chlorinated starches because of the reagent used in  
60 their preparation although no chlorine is chemically bound to the starch). The fluidity and oxidized starches should have a water fluidity (WF) of 5—90, preferably 20—80, and most preferably 35—70. More highly converted starches such as dextrans, even when derivatized, are not suitable for use herein.

In the preparation of the converted starches by acid treatment, the starch base is hydrolyzed in the presence of an acid, such as sulfuric or hydrochloric acid, at a temperature below the gelatinization point of  
65 the starch. The starch is slurried in water, and the acid is then added. Typically, the reaction takes place over

a 8—16 hr. period, after which the acid is neutralized with alkali (e.g. to a pH of 5.5), and the starch recovered by filtration. The resulting converted starch will require cooking to pregelatinize the starch.

In the preparation of the converted starches by enzyme treatment, the starch base is slurried in water, and the pH is adjusted to 5.6—5.7 with alkali or acid. A small amount of alpha amylase enzyme (e.g. about 0.02% on the starch) is added to the slurry, which is then heated above the gelatinization point of the starch. When the desired conversion (W.F.) is reached, the pH is adjusted with acid (e.g. to about 2.0) to deactivate the enzyme and held at that pH for a period of at least 10 minutes. Thereafter the pH may be readjusted upward. The resulting converted starch dispersion is usually jet-cooked to ensure complete solubilization of the starch and deactivation of the residual enzyme.

In the preparation of the converted starches by oxidation with sodium hypochlorite, an aqueous starch suspension (35—44% solids) is usually treated with sodium hypochlorite solution (containing up to about 2% active chlorine) at pH 8—10 and 21—38°C. The reaction is neutralized to pH 5—6.5 when the required level of oxidation (degradation) is reached and excess oxidant is destroyed by addition of sodium bisulfite solution or sulfur dioxide. The reaction product is washed to remove impurities, solubilized starch, and by-products of the reaction either on continuous vacuum filters or in hydrocyclones, recovered by filtration, and dried. The hypochlorite oxidizes a limited number of hydroxyl groups to aldehyde, ketone, and carboxyl groups with concomitant cleavage of the glucoside bonds. The introduction of carboxyl groups into the linear amylose molecules reduces the tendency to gel. Such overstabilization must be avoided for converted starches herein and the previously indicated amount of active chlorine should not be exceeded. The resulting converted starch requires further cooking to pregelatinize the starch.

It will be appreciated that, while the above acid- and enzyme-conversions may be carried out on either the derivatized starch or the underivatized starch, it is common practice to use the underivatized starch.

The converted or converted derivatized starches must be pregelatinized to be useful herein and to form a final cheese product having the desired textural properties. Pregelatinized starches are swellable in cold water without cooking. The starches may be pregelatinized by drum-drying starch slurries directly or after cooking (as in a Votator) or by jet-cooking and spray-drying starch slurries. The cooked starch can be dried by means other than spray-drying (i.e. freeze-drying, alcohol precipitation, rotary evaporation). Other means of carrying out the pregelatinization such as extrusion may also be useful herein. The jet-cooked starch slurries, if desired, can be added directly to the cheese formulation.

Drum-drying is a conventional process for simultaneously cooking and drying starch slurries on heated drums and described in such articles as Chapter XXII—"Production and Use of Pregelatinized Starch", Starch: Chemistry and Technology, Vol. II—Industrial Aspects, R. L. Whistler and E. F. Paschall, Editors, Academic Press, New York 1967. Drum-dried starches are in the form of thin, solid sheets which are pulverized prior to use in the cheese formulation.

Jet-cooking and spray-drying are conventional and described in patents such as US—A—3,674,555. A starch slurry is pumped into a heated cooking chamber where pressurized steam is injected into the starch slurry. The cooked starch solution passes from the cooking chamber and exits via an exit pipe. The starch solution is atomized by pressurized spray nozzles or centrifugal wheel atomizers into a large, heated chamber where the water is evaporated. The starch passes through a cyclone to separate the heated air from the starch powder. The steam-injection, direct spray-drying process and apparatus described in US—A—4,280,851 for gelatinizing starch materials, especially high viscosity materials, in the atomized state is also useful herein.

The preferred starches for use herein are the derivatized fluidity starches and the oxidized starches. Suitable derivatives include esters such as the acetate and half-esters such as the succinate and octenylsuccinate prepared by reaction with acetic anhydride, succinic anhydride and octenylsuccinic anhydride respectively; the phosphate derivative prepared by reaction with sodium or potassium orthophosphate or sodium or potassium tripolyphosphate; ethers such as hydroxypropyl ether prepared by reaction with propylene oxide; and any other edible starch derivatives approved for use in food products. The oxidized starches and derivatized fluidity starches show the gelling and emulsion-stabilizing properties which are preferred for cheese products requiring good shredding and melting characteristics, such as mozzarella cheese.

Each derivative should have the proper treatment level, as indicated herein, to provide the required balance between gel strength and melting characteristics. The amounts of derivatizing reagent currently permitted for use in the preparation of food starches may be above those suitable for use herein. For example, currently the Food and Drug Administration permits the use of up to 25 wt.% propylene oxide. Such a treatment level would not be suitable herein as the resulting starch derivative would be overstabilized and would not provide sufficient gel strength to the cheese product. Likewise, the oxidized starches must be treated at active chlorine levels that do not overstabilize the starch.

The practitioner will recognize that there is a relationship between the derivatizing treatment level required and the water fluidity and amylose content of the starch. Converted starches having a lower water fluidity and higher amylose content form stronger gels and vice versa. The practitioner will also recognize that the gel strength required will vary with the cheese type and its moisture content.

The octenylsuccinate derivatives are preferred when better emulsifying properties are required. The practitioner will recognize that the emulsifying properties required will depend not only on the oil content of the cheese product but the amount of caseinate being replaced, with the octenylsuccinate derivative

being preferred for caseinate replacement levels above 50%. Their use will prevent unacceptable oil loss during preparation of the cheese and undesirable oiling-off on the surface of the final cheese product. Some oiling-off in the melted cheese is desirable. The most preferred starch derivative for use in a mozzarella cheese formulation is a jet-cooked or jet-cooked/spray-dried 35—50 WF corn starch derivative  
 5 treated with 1—2% octenylsuccinic anhydride.

The above starch modification procedures, i.e. conversion, derivatization, and pregelatinization, are conventional and well-known to those skilled in the art and described in such publications as "Handbook of Water-Soluble Gums and Resins", Robert L. Davidson (Editor), Chapter 22: Starch and Its Modifications by M. W. Rutenberg, McGraw Hill Book Co. (New York) 1980.

10 In the preparation of the modified starches, the conversion is typically carried out prior to the pregelatinization step; however, it is possible to pregelatinize the starch prior to conversion. Likewise typically the conversion and derivatization is carried out prior to pregelatinization; however, this sequence can also be reversed with derivatization being carried out prior to conversion.

Highly crosslinked starches generally are not useful herein; for example, a known tapioca-based  
 15 instant gelling starch that has been highly crosslinked after conversion and then drum-dried is unsatisfactory. However, moderate levels of crosslinking which do not adversely effect the gelling of the converted starches are useful herein.

Crosslinking agents suitable for food starches include phosphorus oxychloride, epichlorohydrin, sodium trimetaphosphate, and adipic acid-acetic anhydride (e.g. 1:4). The currently permitted treatment  
 20 levels should provide suitable moderately crosslinked starches when crosslinking agents other than phosphorus oxychloride and epichlorohydrin are used. Such levels include up to 0.04% bound (residual) phosphate, calculated as phosphorus, and up to 0.12% adipic anhydride and up to 2.5% bound acetyl. Of the crosslinking agents discussed above, phosphorus oxychloride is preferred in amounts up to about 0.05%, preferably 0.04% or less, most preferably 0.01%. Treatment with higher levels of phosphorus  
 25 oxychloride (e.g. up to the currently permitted level of 0.1%) provides starches which are too highly crosslinked (i.e. that do not fully cook and/or develop the required viscosity) and form unacceptable cheese products. Treatment with up to 0.3% epichlorohydrin (the currently permitted level) may likewise provide starches which are too highly crosslinked. The above phosphorus oxychloride and epichlorohydrin treatment levels are for non-derivatized converted starches, and it may be possible to use higher treatment  
 30 levels (e.g. 0.06% phosphorus oxychloride) with derivatized starches. The most preferred crosslinked starch derivative for use in a mozzarella cheese formulation is a jet-cooked or jet-cooked/spray-dried 65—70 WF crosslinked corn starch derivative prepared by treatment with up to 0.01% phosphorus oxychloride and 1—2% octenylsuccinic anhydride.

Nonconverted starches (other than the high amylose corn starches which have the required water  
 35 fluidity without conversion) even when pregelatinized or derivatized and pregelatinized, are not useful herein. The use of granular starches (i.e. not pregelatinized), even when converted or converted and derivatized, are also not useful herein. The above starches do not provide the gelling and/or emulsion-stabilizing properties required in the cheese preparation.

The preparation of the imitation cheeses is conventional and well-known to those skilled in the art.  
 40 Methods for the preparation of typical cheese products are described in the following patents:

US—A—4,232,050 and 4,075,360 which disclose methods for the preparation of imitation mozzarella cheeses;

US—A—4,197,322 which describes the preparation of imitation cheeses such as mozzarella and processed American Cheeses;

45 US—A—4,104,413 which describes the preparation of imitation cheeses such as mozzarella and cheddar cheeses;

US—A—3,922,374 which describes a process for the preparation of imitation cheeses such as pasta filata (mozzarella), cheddar, and pasteurized processed American cheeses;

US—A—3,397,994 and US—A—4,166,142 which describe methods for the preparation of imitation  
 50 cream cheese spread and imitation cheese spreads;

US—A—3,502,481 which describes the preparation of cheese-like spreads;

US—A—3,806,606 which describes the preparation of synthetic cheese having the texture and eating quality of natural dairy cheese; and

US—A—4,110,484 which describes a process for the manufacture of acid-set imitation and filled  
 55 cheese products.

The imitation mozzarella cheeses which are functionally equivalent to the caseinate-based imitation cheeses in flavor, texture, and melt and string are typically prepared from 20 to 24% of a vegetable fat or vegetable oils such as corn, sesame, cottonseed, safflower, groundnut, coconut, soybean, olive, palm kernal, and/or wheatgerm oil; from 20 to 30% of a mixture of 20—80% sodium and calcium caseinates (in a  
 60 ratio of about 10 to 90 parts sodium caseinate to about 90 to 10 parts calcium caseinate and 80—20% modified starch; about 42 to 50% water; about 0.5 to 3.0% sodium chloride; about 0.8 to 2.5% trisodium phosphate, sodium aluminum phosphate, and/or calcium phosphate; 0.5 to 2.0% adipic, lactic and/or sorbic acid; and 0.0001 to 1% cheese additives such as butter flavoring; the percentages being by weight.

In imitation mozzarella cheese a mixture of sodium and calcium caseinate is used to provide the final  
 65 stretch, emulsifying, gel and melt properties. Both high sodium and high calcium caseinate systems are

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useful with the modified starches herein. The solubilized caseinates may be formed *in situ* by adding an alkali such as sodium, potassium or calcium hydroxide to dispersions of acid casein (precipitated from milk by the addition of an acid such as hydrochloric or lactic acid) or rennet casein (casein solubilized by reaction with the enzyme rennet).

5 It is surprising that these modified starches can be used as a replacement for all types of caseinates (e.g. sodium, potassium, and calcium caseinate or mixtures thereof) and provide a functionally equivalent imitation cheese product. It is even more surprising that one modified starch can be used even in a cheese such as mozzarella that typically requires a protein mixture (e.g. sodium and calcium caseinate) to provide the shredding, melting and stringing properties of the natural cheese.

10 Typically, the above cheeses are prepared by forming an emulsion of the caseinates, starch, and water with the melted fat or oil and adding the salts and acids at the appropriate times. The mixture is heated during the emulsification and the final plastic mass is compressed and refrigerated for several days.

Imitation processed American and cheddar cheeses have a similar composition except that different salt(s) or acid(s) are used.

15 In the examples which follow, all parts and percentages are given by weight and all temperatures are in degrees Celsius unless otherwise noted. The following testing procedures are used in the examples to characterize the starch products herein.

### Water fluidity measurement

20 The water fluidity of the starches is measured using a Thomas Rotational Shear-Type Viscometer (manufactured by Arthur H. Thomas Co., Philadelphia, PA 19106), standardized at 30°C with a standard oil having a viscosity of 24.73 mPa · s (24.73 cps.), which oil requires 23.12±0.05 sec. for 100 revolutions. Accurate and reproducible measurements of the water fluidity are obtained by determining the time which elapses for 100 revolutions at different solids levels depending on the starch's degree of conversion (as  
25 conversion increases, the viscosity decreases). The procedure used involves slurrying the required amount of starch (e.g., 6.16 g. dry basis) in 100 ml. of distilled water in a covered copper cup and heating the slurry in a boiling water bath for 30 min. with occasional stirring. The starch dispersion is then brought to the final weight (e.g., 107 g.) with distilled water. The time required for 100 revolutions of the resultant dispersion at 81°—83°C. is recorded and converted to a water fluidity number as defined in the table below.

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5	Amount of starch used (anhydrous, g.)	6.16 <sup>a</sup>	8.80 <sup>b</sup>	11.44 <sup>c</sup>	13.20 <sup>d</sup>
		Time required for 100 revolutions (sec.)			Water fluidity
		60.0			5
10		39.6			10
		29.3			15
		22.6			20
15		20.2			25
			33.4		30
20			27.4		35
			22.5		40
				32.5	45
25				26.8	50
				22.0	55
30					24.2 60
					19.2 65
					15.9 70
35					13.5 75
					11.5 80
40					10.0 85
					9.0 90

45      a. b. c. and d. Final weight of starch solutions are 107, 110, 113, and 115 g., respectively.

## Cheese evaluation

50      The cheeses were evaluated for gel strength, emulsion stability during preparation (oil retention or oil loss) and after preparation (oil retention or oiling-off on the cheese surface), and stretch properties by touching and pulling the cheese; for shred by grating the cheese; for melt by heating the grated cheese on a pizza and observing the melt characteristics, i.e. fusion, lack of fusion, or excessive fusion (too much melting resulting in a translucent layer), as well as excessive oil in the melt; and for string by pulling the melted cheese apart. The cheeses were given an overall rating based on the above properties with cheeses which lost oil during their preparation being given a rating of zero. Gel strength and shred were considered

55      the next most important properties. All of the cheeses evaluated were satisfactory in flavor and mouthfeel. A rating below 5 was considered unsatisfactory. The control cheeses were given an automatic rating of 10 even though the high sodium caseinate formulation was inferior to the high calcium caseinate formulation in string, melt, and stretch. Acceptable cheeses (i.e. functionally equivalent) had a rating of at least 5, with the substantially equivalent and equivalent mozzarella cheeses having ratings of 8—9.5.

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## Example 1

This example describes the preparation of imitation mozzarella cheeses, based on high sodium and high calcium caseinate formulations, containing jet-cooked/spray-dried 40 WF corn starch octenylsuccinate derivatives at 50% replacement.

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## Preparation of the modified starch

A slurry of 100 parts of granular corn starch in 150 parts of water was heated in a water bath to 52°C, 0.5 parts of hydrochloric acid were added, and the mixture was stirred for 16 hours at 52°C. The hydrolysis was stopped by neutralizing the mixture with alkali (a solution of 3% sodium hydroxide) to a pH of 5.5. The converted starch was recovered by filtration, washed and dried; it showed a water-fluidity of 40, as measured by the test procedure described above.

A total of 100 parts of the converted starch was slurried in 150 parts of water, the pH was adjusted to 7.5 with sodium hydroxide and the indicated amount (1% and 3%) of octenylsuccinic anhydride (OSA) was added slowly while the pH was maintained at 7.5 with sodium hydroxide. The reaction was complete when no further addition of alkali was necessary. The pH was then adjusted to 5.5 with acid. The resulting octenylsuccinate derivatives were recovered by filtration and washed.

A total of 100 parts of the derivatized starch was then slurried in 233 parts of water and passed through a continuous steam jet-cooker at 138°C. The resulting starch solution was spray-dried at a chamber temperature of 210°C and an outlet temperature of 90°C.

## Preparation of the cheeses

The cheeses were prepared by dry blending the caseinates (control cheese) or caseinates and starch (replacement cheese) at low speed in a Hobart mixer. The melted shortening or oil was blended in and mixing was continued for 3 minutes. About 1/2 of the mixture was removed and, while continuing agitation, about 85% of the water was added. Mixing was continued for about 1 minute until the emulsion was homogeneous. The removed shortening/caseinate/starch mixture was added and agitation was continued for about 2 minutes. Sorbic acid and the setting salts were then added at medium speed and mixing was continued until the mixture was homogeneous. The adipic acid and remaining water were added and mixed in. The resulting cheeses were removed, pressed slightly to firm the mixture, and refrigerated at 4°C (40°F) for 1—3 days. The laboratory preparation, wherein the remaining water is post-added after the sorbic acid and setting salts, simulates a typical commercial preparation wherein steam is injected into the final mixture after the acid and salt addition.

The control cheeses and cheeses containing the modified starches were formulated as follows:

Ingredient (parts)	Cheese formulation <sup>a</sup>		Cheese formulation <sup>b</sup>	
	(Control)	(Starch replacement)	(Control)	(Starch replacement)
Sodium Caseinate	21.2	10.6	5.4	2.7
Calcium Caseinate	5.4	2.7	21.2	10.6
Modified Starch <sup>c</sup>	—	13.3	—	13.3
Shortening	22.8	22.8	22.6	22.6
Sodium Chloride	0.9	0.9	0.9	0.9
Trisodium Phosphate	0.3	0.3	0.3	0.3
Sodium Aluminum Phosphate	0.3	0.3	0.3	0.3
Calcium Phosphate	0.3	0.3	0.3	0.3
Adipic Acid	0.3	0.3	0.3	0.3
Sorbic Acid	0.3	0.3	0.3	0.3
Water	48.5	48.5	48.5	48.5
	100.3	100.3	100.1	100.1

<sup>a</sup> High Sodium Caseinate—70%/30% Na/Ca caseinate

<sup>b</sup> High Calcium Caseinate—70%/30% Ca/Na caseinate

<sup>c</sup> 40 WF Corn; 1% & 3% OSA; jet-cooked (JC)/spray-dried (SD).

The cheese evaluations are summarized in Table I.



TABLE I

Cheese	Caseinate replacement level (%)	Gel	Shred	Emulsion stability	String	Melt	Stretch	Overall <sup>a</sup> rating
High Na Caseinate Control	0%	Firm	V. Good	V. Good	Poor <sup>d</sup>	Poor <sup>a</sup>	Poor <sup>d</sup>	10
High Na Caseinate/Starch <sup>a</sup>	50%	Soft	Good	Good	Good	Good	Good	8
High Ca Caseinate Control	0%	Firm	V. Good	Good	Good	Good	Good	10
High Ca Caseinate/Starch <sup>a</sup>	50%	Firm	Fair	Good	Good	Good	V. Good	8
High Ca Caseinate/Starch <sup>b</sup>	50%	Firm	Good	Good	Good	Good	Good	9

<sup>a</sup>. 40 WF Corn; 3% OSA; JC/SD<sup>b</sup>. 40 WF Corn; 1% OSA; JC/SD<sup>c</sup>. No fusion of grated cheese pieces<sup>d</sup>. Too short<sup>e</sup>. The controls were given an automatic rating of 10 despite the differences in the properties of the high sodium and high calcium caseinate cheeses.

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The results show that, in the high sodium caseinate cheese formulation, the product containing the modified starch was better than the control in stretch, string, and melt but poorer in gel strength. In the high calcium caseinate cheese formulation, the products containing the starch were both excellent, with the 1% OSA derivative being better in shred but poorer in melt than the 3% OSA derivative. The high caseinate control was only slightly better in one property (i.e. shred). It is thus demonstrated that the imitation mozzarella cheese products containing the modified starches as partial replacements for both sodium and calcium caseinate were functionally equivalent to the controls for both the high sodium and high calcium caseinate cheese formulations. Similar cheese products were prepared using olive oil, partially hydrogenated soy bean oil, and various solidified hydrogenated vegetable oils with comparable results.

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### Example II

This example demonstrates the use of starches prepared from other starch bases, as well as the use of starches of varying water fluidities as caseinate replacements.

The derivatized starches were treated with 3% OSA and jet-cooked and spray-dried according to the procedure described in Example I. The non-derivatized starches were jet-cooked and used directly in the formulation; in these cheese formulations the added water was adjusted to provide the required starch solids content. They were evaluated in the above high calcium caseinate cheese formulation at a 50% replacement level. The overall rating of the various replacement starches are summarized below.

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	Starch <sup>a</sup>	Cheese overall rating
	40 WF Corn; JC	7
25	20 WF Corn; 3% OSA; JC/SD	8
	80 WF Corn; 3% OSA; JC/SC	7
30	40 WF Potato; JC	7.5
	20 WF Potato; 3% OSA; JC/SD	7
	80 WF Potato; 3% OSA; JC/SD	0
35	40 WF Tapioca; JC	7
	20 WF Tapioca; 3% OSA; JC/SD	6
40	80 WF Tapioca; 3% OSA; JC/SD	0
	40 WF Amioca; JC	2
45	20 WF Amioca; 3% OSA; JC/SD	4
	80 WF Amioca; 3% OSA; JC/SD	0

50 <sup>a</sup> The amylose content of the starches was about 21—28% for corn, 23% for potato, 17—22% for tapioca, and <1% for Amioca (a waxy maize starch).

The results show that the products containing the non-derivatized starches were good for all bases except Amioca. The cheeses had the following properties: firm gel; good shred and emulsion; and fair to good stretch, string, and melt.

The results also show that the products containing the starch derivatives based on Amioca were likewise unacceptable (ratings of 4 and 0); the gel was very soft, and shred was fair to poor (matted) and, in addition, the 80 WF derivative lost considerable oil (50 cc).

60 The results further show that potato and tapioca starch derivatives having high viscosities (20 WF) were satisfactory. The 20 WF potato and tapioca starch derivatives provided products which were slightly softer in gel and somewhat poorer in shred than the product prepared with the 20 WF corn starch derivative. The 80 WF starch derivatives all gave cheese products with slightly softer gels, and the products containing the potato and tapioca starch derivatives were unacceptable having oil losses of 45 and 41 cc, respectively. The cheese prepared with the 80 WF corn derivative did not lose oil.

## Example III

This example demonstrates the effect of derivatization (type and amount) on the starches.

## Part A

- 5 Various starch derivatives having approximately the same degree of substitution (about 0.0078) were prepared using the indicated amounts of derivatizing reagent to treat a 40 WF fluidity corn starch. The derivatives were jet-cooked and spray-dried as before and evaluated at a 50% replacement level in the high calcium caseinate cheese formulation. The overall ratings are shown below.

10	Modified starch	Overall cheese rating
	40 WF Corn; 1% OSA; JC/SD <sup>a</sup>	9
	40 WF Corn; 0.28% PO; JC/SD <sup>b</sup>	6
15	40 WF Corn; 0.50% Ac <sub>2</sub> O; JC/SD <sup>c</sup>	5
	40 WF Corn; JC/SD	7
20	<sup>a</sup> . The derivative was prepared using the indicated amount of octenylsuccinic anhydride as described in Example I.	
	<sup>b</sup> . The derivative was prepared by slurrying 100 parts of the starch into a solution of 30 parts sodium sulfate in 150 parts water, adding 1.5 parts sodium hydroxide, and then adding indicated amount of propylene oxide (PO). The slurry was agitated for 16 hours at 40°C in a sealed vessel. When the reaction was completed, the pH was adjusted to 5.5 with acid. The derivative was recovered by filtration, washed, and air dried.	
25	<sup>c</sup> . The derivative was prepared by slurrying 100 parts of the starch in 150 parts water, adjusting the pH to 8.3 with 3% sodium hydroxide solution, and slowly adding the indicated amount of acetic anhydride (Ac <sub>2</sub> O) while maintaining the pH at 8.3 with the above alkali; the pH was then adjusted to 5.5 with acid. The reaction was complete when no further addition of alkali was necessary. The derivative was recovered as hereinabove.	
30		

- The results show that all the derivatives gave acceptable products with the octenylsuccinate being the best. The acetate and hydroxypropyl starch derivatives formed products with softer gels but no oil loss occurred. Their shredding characteristics were poor (matting) in comparison with the product containing the octenylsuccinate starch derivative. The products also showed to much melt. The results also show that the non-derivatized converted starch gave a product which was acceptable (firm gel; fair emulsion, stretch, and string; good shred; fair melt). It would appear the non-derivatized, converted starches will be most useful in cheeses requiring good gel strength and shred rather than cheeses such as mozzarella which have rigid melting requirements including string.

## Part B

- 45 Various octenylsuccinate derivatives were prepared using the indicated amounts of octenylsuccinic anhydride to treat both high viscosity (20 WF) and low viscosity (80 WF) fluidity corn starches. The derivatized starches and the non-derivatized 20 WF starch were jet-cooked and spray dried as above; the 80 WF corn was jet-cooked at the indicated temperature and used without spray-drying as described in Example II. The starches were evaluated at a 50% replacement level in the high calcium caseinate cheese formulation. The overall ratings are given in Table II.

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TABLE II

Starch	Gel	Shred	Emulsion stability	String	Melt	Stretch	Overall rating
20 WF Corn; JC/SD	Firm	Good	Poor*	Poor	Poor	Poor	5
20 WF Corn; 0.5% OSA; JC/SD	Firm	Good	Good	Fair	Fair	Fair	9
20 WF Corn; 1.0% OSA; JC/SD	Firm**	Good	Good	Good	Good	Good	8.5
20 WF Corn; 2.0% OSA; JC/SD	Firm**	Good	Good	Good	Good	Good	8
20 WF Corn; 3.0% OSA; JC/SD	Soft	Fair—Good	Good	Fair	Poor***	Good	5
80 WF Corn; JC at 300°F/SD	Soft	Poor	Poor****	Good	Excellent	Good	0
80 WF Corn; 0.25% OSA; JC at 300°F/SD	Soft	Poor	Poor****	Good	Excellent	Good	0
80 WF Corn; 1.00% OSA; JC at 300°F/SD	Soft	Poor	Good	Good	Excellent	Good	5

\* Oiling off on the cheese surface after storage.

\*\* The gels of the cheeses containing the 1% and 2% OSA starch derivatives were slightly less firm and less firm than those of the cheese containing the 0.5% OSA starch derivative and hence the products were given slightly lower overall ratings.

\*\*\* Fused to well, runny & transparent.

\*\*\*\* 40 cc oil loss with no OSA; 20 cc oil loss with 0.25% OSA vs. no oil loss with 1.00% OSA.

The results show that the 20 WF starches gave acceptable cheese products with firm gels and good shredding characteristics. Treating the starches with low levels of OSA improved the cheese properties. However, increasing the treatment level to 3% OSA adversely affected both the melt (excessive fusion) and the string (fair) and shred (good to fair). As the OSA treatment level was increased from 0.5% to 1% the stretch, string, and melt improved from fair to good. The non-derivatized 20 WF starch gave an acceptable cheese product which was good in shred but poor in emulsion, stretch, string and melt.

The results further show the derivatization with a high enough level of octenylsuccinic anhydride (1%) improved the overall rating (0 to 5) for the cheese containing the spray-dried 80 WF starch. Specifically, the oil loss was eliminated even though the gel strength remained unchanged. The cheeses containing the derivatized 80 WF starches had soft rather than firm gels; they were better in melt (excellent vs. good) but poorer in shred (poor vs. very good) than the control cheese (see Example I).

The above results indicate that the octenylsuccinate modified starches serve a dual purpose in the cheese, i.e. they stabilize the amylose to improve melt quality and more importantly they aid in the emulsification of the fat during the cheese preparation. Hence, these derivatives are preferred if both emulsification and meltability must be improved. They are also preferred for caseinate replacement levels above 50% and preferred for cheeses, such as mozzarella.

#### Example IV

This example shows the use of oxidized starches and mildly cross-linked derivatized starches as caseinate replacements in the high calcium caseinate cheese formulation. It also establishes the maximum active chlorine level acceptable in the oxidative treatment and the maximum phosphorus oxychloride treatment levels for the crosslinked derivatized starches.

#### Part A

The starches were prepared by slurring 100 parts of the starch in 150 parts water and adjusting the pH to 5.5 with acid or alkali. The starch slurry was placed in insulated jars and the alkaline sodium hypochlorite solution containing the indicated level of active chlorine was slowly added over a 90 minute period. The reaction was carried out over a 16 hour period at room temperature. Any excess chlorine was neutralized with a solution of sodium bisulfite, the pH was adjusted to 5.5 with acid, and the oxidized starch was recovered by filtration, washed, and dried. The water fluidity of the oxidized starches is given below. The cheese evaluation results were as follows:

	Starch (19% solids in the cheese)	Replacement level	Overall rating
35	42 WF Potato; 0.5% Cl <sub>2</sub>	50%	8.5
	78 WF Potato; 1.5% Cl <sub>2</sub>	50%	8
	84 WF Potato; 2.5% Cl <sub>2</sub>	50%	4
40	84 WF Potato; 3.5% Cl <sub>2</sub>	50%	3

The results show that when the oxidized starches were not over-stabilized they gave good products. The 42 WF starch gave a firm gel, good emulsion, good shred, fair stretch, and good melt. The 78 WF starch was slightly softer in gel strength and slightly better in melt and stretch. The higher fluidity starches, even though they lost no oil, had soft gels with very poor shredding (wet matted) and poor melting (excessive fusion) characteristics.

#### Part B

The starches were prepared by slurring 100 parts of the starch in 150 parts water and adding 0.8% sodium hydroxide and 1% sodium chloride (based on the dry starch) and the indicated amount of phosphorus oxychloride. The reaction was carried out over a 3 hour period at room temperature, the pH was adjusted to 5.5 with acid, and the crosslinked starch was recovered by filtration, washed, and dried. The crosslinked starches were modified by treatment with the indicated amount of OSA as in Example I but were used directly after jet-cooking (without spray-drying) in the cheeses. The cheese evaluation results were as follows:

	Starch (19% solids in the cheese)	Replacement level	Overall rating
60	67 WF Corn; 0.01% POCl <sub>3</sub> 1.5% OSA; (final WF 40); JC	50%	8.5
	67 WF Corn; 0.05% POCl <sub>3</sub> 1.5% OSA; (final WF 20); JC	50%	6
	70 WF Corn; 0.07% POCl <sub>3</sub> ; 1.5% OSA; (final WF 25); JC	50%	2
65	70 WF Corn; 0.10% POCl <sub>3</sub> 1.5% OSA; (final WF 31); JC	50%	4

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The results show that the crosslinked derivatized starches gave acceptable cheese products provided the treatment level was below 0.07%.

### Part C

5 The starch evaluated was a lightly converted, lightly crosslinked, drum-dried (DD) starch. The cheese evaluation results were as follows:

	Modified starch	Replacement level	Overall cheese rating
10	27 WF Tapioca; 0.015% POCl <sub>3</sub> ; DD	30%	7
	27 WF Tapioca; 0.015% POCl <sub>3</sub> ; DD	50%	4

15 The results show that at 30% replacement an acceptable could be prepared. At 50% replacement the cheese was unacceptable; however, at this level the use of a more highly converted (higher WF) crosslinked starch would likely provide an acceptable cheese with a firmer gel and better shred.

### Example V

20 This example demonstrates that the modified starch (40 WF corn; 1% OSA) must be pregelatinized. The starches evaluated (50% replacement in the high calcium caseinate cheese formulation) included the converted, derivatized starch in the granular state and in the pregelatinized dry form. The overall rating of the cheeses are given below.

	Modified starch	Overall cheese rating
25	40 WF Corn; 1% OSA (granular)	4
	40 WF Corn; 1% OSA; DD	7
30	40 WF Corn; 1% OSA; JC/SD	8

35 The results show that the granular starch gave an unacceptable cheese product. Even though the gel was firm and the emulsion, stretch and string were good, the product's texture was poor (i.e. grainy) and, in addition, the melt and shred were only fair. In comparison, all of the cheeses containing pregelatinized modified starches were acceptable. The cheese containing the drum-dried (D.D.) starch was almost as good as that containing the jet-cooked/spray-dried starch (the gel, emulsion, and shred were good for both cheeses but the stretch, string, and melt were only fair with the drum-dried starch). See Example I for the specific properties of the Control cheese and the product containing 40 WF Corn; 1% OSA; JC/SD starch as the caseinate replacement.

### 40 Example VI

45 This example shows the influence of starch amylose content on the cheese properties. The blends were formulated from a 40 WF Amioca (approximately 0% amylose) and 40 WF corn (approximately 27% amylose) to give the indicated amylose content. They were evaluated at 50% replacement in the high calcium caseinate formulation. For comparison, the results obtained using a jet cooked 40 WF Amioca are included.

	Starch	
	Modification/blend	Amylose content (%)*
50		Overall cheese rating
	40 WF Amioca; JC	0
		2
55	40 WF Amioca/40 WF Corn; JC	5
		3
	40 WF Amioca/40 WF Corn; JC	10
		4
	40 WF Amioca/40 WF Corn; JC	15
		5
60	40 WF Amioca/40 WF Corn; JC	20
		7

\* Approximate

65 The results show that there is a minimum amylose content (above 10%) that must be present to provide an acceptable cheese product and that blends having this amylose content are useful herein. The

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cheese product prepared with the 40 WF Amioca had a very soft gel, very poor shred (mating) and poor melt (excessive). At 5% amylose the melt was improved (not as runny), but the gel and shred were still very poor. At 10% amylose the product began to resemble cheese; the melt was good but the gel was still poor and matting was still a problem. At 15% amylose melt was good, gel and shred were acceptable, but string had been reduced from good to fair. At 20% amylose the gel strength was very firm (firmer than the control cheese), shred was excellent, but melt and string were only fair.

## Example VII

This example shows the use of the octenylsuccinate starch derivative at various replacement levels in the high calcium caseinate cheese formulation. The overall rating for the cheeses was as follows:

	Modified starch	Replacement level	Overall cheese rating
15	40 WF Corn; 1% OSA; JC/SD	25%	9.5
	40 WF Corn; 1% OSA; JC/SD	50%	9
	40 WF Corn; 1% OSA; JC/SD	75%	7
20	40 WF Corn; 1% OSA; JC/SD	100%	3

The results show that at 25% replacement the cheese was equivalent to the control cheese (see Example I) in all properties (firm gel; very good shred; good melt; and good string). At 50% replacement the cheese was excellent and functionally equivalent; it was only slightly inferior in shred (good vs. very good). At 75% replacement the cheese was still very good and nearly equivalent (slightly soft gel; good stretch; fair shred with some matting; and fair melt). At 100% replacement the cheese-like product formed was unacceptable; it was crumbly and poor in all properties.

## Example VIII

This example illustrates the use of the preferred caseinate-replacement starch at 50% replacement in other cheese formulations. The control cheeses and starch-containing cheeses were formulated as in Example I using the following ingredients:

Ingredient (parts)	Imitation processed American cheese		Imitation cheddar cheese	
	(Control)	(Replacement)	(Control)	(Replacement)
Calcium caseinate	20.0	10.0	21.0	10.5
40 Sodium caseinate	5.0	2.5	5.0	2.5
Modified starch*	—	12.5	—	13.0
45 Shortening	28.1	28.1	32.3	32.3
Salt	2.0	2.0	2.2	2.2
Sodium aluminum phosphate	0.9	0.9	0.5	0.9
50 Citric acid	0.5	0.5	0.9	0.5
Sodium citrate	0.2	0.2	0.4	0.4
55 Cheese flavoring	—	—	—	—
Cheese coloring	—	—	—	—
Water	43.3	43.3	37.6	37.6
60	100.0	100.0	100.0	100.0

\* 40 WF Corn; 1% OSA; JC/SD

The cheeses were evaluated as before; the rating of the imitation and replacement mozzarella cheeses are included for comparison with the results given in Table III.

TABLE III

Imitation cheese	(type)	Gel	Shred	Emulsion stability	String	Melt	Stretch	Overall rating
Control	(Mozzarella)	Firm	Good	Good	Good	Good	Good	10
Replacement	(Mozzarella)	Firm	Good	Good	Good	Good	Good	8
Control	(American)	Firm	None	Excellent	Good	Excellent	None	10
Replacement	(American)	Sl. Soft	None	Good	Good	Good	None	7
Control	(Cheddar)	V. Firm	None	Fair	Fair	Good	None	10
Replacement	(Cheddar)	Sl. Soft	Fair	Fair	Fair	Good	Good	6



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The results show that the caseinate-replacement starch can be used in other types of imitation cheeses to give an acceptable product.

### Example IX

5 This example shows the effect of starch viscosity and demonstrates that dextrins and non-converted starch can not be used in the formulations.

The starches evaluated included fluidity corn starch derivatives, a non-converted OSA starch derivative, spray-dried corn dextrins, and spray-dried OSA corn dextrin derivatives. They were evaluated at 50% replacement in the high calcium caseinate mozzarella cheese formulation. The cheese properties and  
10 ratings are given in Table IV.

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TABLE IV  
Cheese properties

Modified starch	Cheese properties						Overall rating
	Gel	Shred (matts)	Emulsion stability (cc. oil loss)	Stretch	Melt	String	
Corn; 1% OSA; JC/SD	V. Soft	Poor (matts)	Poor (20)	Poor	Poor	Poor	0
20 WF Corn; 1% OSA; JC/SD	Sl. Soft	Fair	Good	Fair	Fair	Fair	7
40 WF Corn; 1% OSA; JC/SD	Firm	Good	Good	Good	Good	Good	9
60 WF Corn; 1% OSA; JC/SD	Sl. Soft	Fair	Good	Excellent	Excellent	Excellent	6
80 W Corn; 1% OSA; JC/SD	Poor	Poor	Good	Good	Good	Good	5
Corn Dextrin; Low Conversion <sup>a</sup>	V. Soft	Poor	Poor (36)	Fair	Good	Fair	0
Corn Dextrin; Medium Conversion <sup>b</sup>	V. Soft	Poor	Poor (50)	Fair	Good	Fair	0
Corn Dextrin; High Conversion <sup>b</sup>	V. Soft	Poor	Poor (62)	Fair	Good	Fair	0
Corn Dextrin; Low Conversion; 3% OSA <sup>a</sup>	V. Soft <sup>c</sup>	Poor	Poor (30)	Poor	Fair	Poor	0
Corn Dextrin; Medium Conversion; 3% OSA <sup>b</sup>	V. Soft <sup>c</sup>	Poor	Poor (40)	Poor	Fair	Poor	0
Corn Dextrin; High Conversion; 3% OSA <sup>b</sup>	V. Soft <sup>c</sup>	Poor	Poor (50)	Poor	Fair	Poor	0

<sup>a</sup>. Corn dextrin and derivatized corn dextrin (spray-dried) having water fluidities of 80 WF.

<sup>b</sup>. Medium and high conversion corn dextrins and derivatized corn dextrins (spray-dried) which were even lower in viscosity than the low conversion dextrins; their water fluidities could not be determined.

<sup>c</sup>. Softer than the non-derivatized spray-dried corn dextrins of comparable viscosities.

The results show that to obtain the best gel strength for the cheese it is necessary to lower the molecular weight of the starch by conversion. This is demonstrated by the fact that the gel of the non-converted octenylsuccinate derivative was very soft and an oil loss of 20 cc. resulted. The cheese was unacceptable in both its properties and because of this oil loss. The fluidity (converted) starches all produced acceptable cheese products with the 40 WF starch showing the firmest gel and best overall properties.

The corn dextrins and OSA-derivitized corn dextrins gave unacceptable cheese products with a very soft gel, unacceptable oil losses (36—62 cc), and fair to poor cheese characteristics.

#### 10 Example X

This example demonstrates that not all pregelatinized starches can be used as caseinate replacements even though they may be known to have gelling properties. The starches evaluated at 50% replacement in the high calcium caseinate cheese formulation included an overstabilized crosslinked tapioca starch (7.5% propylene oxide) known to be useful as a gelling agent in puddings and pie fillings and an overstabilized tapioca starch (above 2% available chlorine) having the required WF. The overall cheese ratings are given below.

	Modified starch	Cheese rating
20	Tapioca treated with 7.5% propylene oxide; crosslinked with 0.008% phosphorus oxychloride; drum dried	0
25	Tapioca oxidized with 3.5% available chlorine; derivitized with 5% acetic anhydride; jet-cooked and spray-dried.	4

The results show that the overstabilized lightly crosslinked starch is not suitable for use herein. The cheese prepared using this non-converted starch lost 20 cc. of oil; the gel was very soft; and the shred was not only matted but breadly. The results also show that overstabilized oxidized starches (80 WF) are not suitable for use herein. The resulting cheese had a very soft gel; the shred was matted; and the melt was only fair (too much oil release).

Summarizing, imitation cheese products, functionally equivalent to caseinate-based imitation cheese products, which contain selected modified starches as a partial replacement for the caseinates are provided. An imitation mozzarella cheese, equivalent in such properties as shred, melt, and string, which contains a converted octenylsuccinate corn starch as the caseinate replacement is also provided.

#### Claims

40 1. An imitation cheese product containing at least one edible caseinate, characterized in that up to 80% by weight of the caseinate is replaced by an edible modified starch; the starch being a pregelatinized converted starch having a water fluidity (WF) of 5—90 and an amylose content of at least 15% and less than 40% by weight, or the derivatives thereof prepared by treatment with up to about 10% propylene oxide, up to about 2% succinic anhydride, or up to about 3% octenylsuccinic anhydride, or with a sufficient amount of acetic anhydride to provide a maximum of about 2.5% bound acetyl, or with a sufficient amount of sodium or potassium orthophosphate, sodium or potassium tripolyphosphate, or mixtures thereof to provide a maximum of about 0.4% bound phosphate, or the moderately crosslinked products thereof prepared by treatment with phosphorus oxychloride, epichlorohydrin, sodium tri-metaphosphate, or adipic-acetic anhydride, or the derivitized moderately crosslinked starches; the converted starch being a fluidity starch prepared by treatment with acid or enzyme or an oxidized starch prepared by treatment with up to about 2% active chlorine; the treatment percentages being by weight based on the starch; whereby the starch-caseinate cheese product is functionally equivalent to the caseinate-based imitation cheese product.

55 2. The product of Claim 1, characterized in that the caseinate is sodium, potassium or calcium caseinate or mixtures thereof; and characterized in that the pregelatinized starch is a drum dried, jet-cooked, or jet-cooked, spray-dried starch, the starch being corn, potato, or tapioca starch or mixtures thereof with a waxy starch, the starch mixtures having a total amylose content of about 15% or above.

60 3. The product of Claim 2, characterized in that the starch has an amylose content of about 20 to 30% and is a 20—80 WF corn, potato or tapioca starch or a derivative thereof prepared by treatment with 1—3% octenylsuccinic anhydride, 0.25—2% propylene oxide, or with a sufficient amount of acetic anhydride to provide 0.13—1.6% bound acetyl; or is a 40—80 WF potato starch prepared by treatment with 0.5—1.5% active chlorine.

65 4. The imitation cheese product of Claim 1, characterized in that the caseinate is a mixture of sodium and calcium caseinate of which 25—75% is replaced with the starch; whereby the starch-caseinate cheese

product is functionally equivalent to the caseinate-based imitation mozzarella cheese, cheddar cheese, or processed American cheese product.

5 The product of Claim 4, characterized in that the ratio of sodium to calcium caseinate is from 30:70 to 70:30 and in that the caseinate is replaced with 25—50% of the starch; and characterized in that the starch is a drum-dried, jet-cooked, or jet-cooked, spray-dried corn, potato, or tapioca starch or mixtures thereof with a waxy starch, the starch mixtures having a total amylose content of at least 15% or above.

6 The product of Claim 5, characterized in that the starch is a 20—80 WF corn, potato, or tapioca starch or a derivative thereof prepared by treatment with 1—3% octenylsuccinic anhydride, 0.25—2% propylene oxide, or a sufficient amount of acetic anhydride to provide 0.13—1.6% bound acetyl; or is a 40—80 WF potato starch prepared by treatment with 0.5—1.5% active chlorine; or is a 20—80 WF corn, potato, or tapioca starch crosslinked with up to 0.06% phosphorus oxychloride and derivatized by treatment with up to 3% octenylsuccinic anhydride or up to 2% propylene oxide.

7 The product of Claim 4, characterized in that the caseinate is a mixture of 70% sodium caseinate and 30% calcium caseinate or of 30% sodium caseinate and 70% calcium caseinate of which 25—50% is replaced by the starch; and characterized in that the starch is a 20—80 WF corn, potato, or tapioca starch or a derivative thereof prepared by treatment with 1—3% octenylsuccinic anhydride, 0.25—2% propylene oxide, or with a sufficient amount of acetic anhydride to provide 0.13—1.6% bound acetyl; or is a 40—80 WF potato starch prepared by treatment with 0.5—1.5% active chlorine; whereby the starch-caseinate cheese product is functionally equivalent to the caseinate-based imitation mozzarella cheese product.

8 The product of Claim 7, characterized in that the starch is a 40—60 WF corn starch derivative prepared by treatment with 1—3% octenylsuccinic anhydride; or is a 40—80 WF potato starch prepared by treatment with about 0.5—1.5% active chlorine; or is a 60—70 WF crosslinked corn starch derivative prepared by treatment with up to 0.05% phosphorus oxychloride and up to 1.5% octenylsuccinic anhydride; whereby the starch-caseinate cheese product is substantially equivalent in shred, melt, and string to the caseinate-based imitation mozzarella cheese product.

9 The product of Claim 7, characterized in that the caseinate mixture is 30% sodium caseinate and 70% calcium caseinate; and characterized in that the starch is a 35—50 WF corn starch derivative prepared by treatment with a 1—2% octenylsuccinic anhydride; or is a 65—70 WF crosslinked corn starch derivative prepared by treatment with up to 0.01% phosphorus oxychloride and 1—2% octenylsuccinic anhydride; whereby the starch-caseinate cheese product is equivalent in shred, melt, and string to the caseinate-based imitation mozzarella cheese product.

10 A method for preparing the imitation cheese product of Claim 1 from water, a melted vegetable fat or a vegetable oil, an edible caseinate, cheese additives, and the edible modified starch, characterized in that the water and melted fat or oil are gelled and emulsion-stabilized by the caseinate-starch mixture.

#### Patentansprüche

1. Käseähnliches Produkt mit einem Gehalt an mindestens einem genießbaren Kaseinat, dadurch gekennzeichnet, daß bis zu 80 Gew.-% des Kaseinats ersetzt sind durch eine genießbare modifizierte Stärke, wobei die Stärke bedeutet eine eine Wasserfluidität (WF) von 5 bis 90 und einen Amylosegehalt von mindestens 15 und weniger als 40 Gew.-% aufweisende vorgelierte umgewandelte Stärke oder Derivate davon, hergestellt durch Behandlung mit bis zu etwa 10% Propylenoxid, bis zu etwa 2% Bernsteinsäureanhydrid oder bis zu etwa 3% Octenylbernsteinsäureanhydrid oder mit einer ausreichenden Menge Essigsäureanhydrid, um ein Maximum von etwa 2,5% an gebundenem Acetyl zu erhalten, oder mit einer ausreichenden Menge an Natrium- oder Kaliumorthophosphat, Natrium- oder Kaliumtripolyphosphat oder Mischungen davon, um ein Maximum von etwa 0,4% an gebundenem Phosphat zu erhalten, oder die mäßig vernetzten Produkte davon, hergestellt durch Behandlung mit Phosphoroxchlorid, Epichlorhydrin, Natriumtrimetaphosphat oder Adipinsäure-Essigsäure-Anhydrid, oder die derivatisierten mäßig vernetzten Stärken, wobei die umgewandelte Stärke eine Fluiditätsstärke ist, hergestellt durch Behandlung mit Säure oder Enzym, oder eine oxidierte Stärke ist, hergestellt durch Behandlung mit bis zu etwa 2% an aktivem Chlor, wobei die auf die Behandlung zurückgehenden Prozentangaben auf das Gewicht, bezogen auf die Stärke, abstellen und das Stärke-Kaseinat-Käseprodukt dem käseähnlichen Produkt auf der Basis von Kaseinat funktionell gleichwertig ist.

2. Produkt nach Anspruch 1, dadurch gekennzeichnet, daß das Kaseinat Natrium-, Kalium- oder Calciumkaseinat oder Mischungen davon ist und dadurch gekennzeichnet, daß die vorgelierte Stärke eine walzengetrocknete, strahlgekohte oder strahlgekohte, sprühgetrocknete Stärke ist, wobei die Stärke Mais-, Kartoffel- oder Tapiokastärke oder Mischungen davon mit einer Wachsstärke ist und die Stärkemischungen einen Amylosegesamtgehalt von etwa 15% oder mehr aufweisen.

3. Produkt nach Anspruch 2, dadurch gekennzeichnet, daß die Stärke einen Amylosegehalt von etwa 20 bis 30% hat und eine eine Wasserfluidität von 20 bis 80 aufweisende Mais-, Kartoffel- oder Tapiokastärke oder ein Derivat davon ist, hergestellt durch Behandlung mit 1 bis 3% Octenylbernsteinsäureanhydrid, 0,25 bis 2% Propylenoxid oder mit einer ausreichenden Menge an Essigsäureanhydrid, um 0,13 bis 1,6% gebundenes Acetyl zu schaffen, oder eine eine Wasserfluidität von 40 bis 80 aufweisende Kartoffelstärke ist, hergestellt durch Behandlung mit 0,5 bis 1,5% an aktivem Chlor.

4. Käseähnliches Produkt nach Anspruch 1, dadurch gekennzeichnet, daß das Kaseinat eine Mischung

aus Natrium- und Calciumkaseinat ist, von dem 25 bis 75% durch Stärke ersetzt worden sind, wodurch das Stärke-Kaseinat-Käseprodukt dem auf Kaseinat beruhenden mozarellakäseähnlichen Produkt, Cheddar-Käse oder behandelten amerikanischen Käseprodukt funktionell gleichwertig ist.

5 5. Produkt nach Anspruch 4, dadurch gekennzeichnet, daß das Verhältnis von Natrium- zu Calciumkaseinat zwischen 30:70 und 70:30 liegt und daß das Kaseinat durch 25 bis 50% Stärke ersetzt worden ist und dadurch gekennzeichnet, daß die Stärke eine walzengetrocknete, strahlgekochte oder strahlgekochte, sprühgetrocknete Mais-, Kartoffel- oder Tapiokastärke oder Mischungen davon mit einer Wachsstärke ist, wobei die Stärkemischungen einen Amylosegesamtgehalt von mindestens 15% oder mehr aufweisen.

10 6. Produkt nach Anspruch 5, dadurch gekennzeichnet, daß die Stärke eine Wasserfluidität von 20 bis 80 aufweisende Mais-, Kartoffel- oder Tapiokastärke oder ein Derivat davon ist, hergestellt durch Behandlung mit 1 bis 3% Octenylbernsteinsäureanhydrid, 0,25 bis 2% Propylenoxid oder einer ausreichenden Menge an Essigsäureanhydrid, um 0,13 bis 1,6% gebundenes Acetyl zu schaffen, oder eine Wasserfluidität von 40 bis 80 aufweisende Kartoffelstärke ist, hergestellt durch Behandlung mit 0,5 bis 1,5% an aktivem Chlor, oder eine Wasserfluidität von 20 bis 80 aufweisende Mais-, Kartoffel- oder Tapiokastärke ist, vernetzt mit bis zu 0,06% Phosphoroxychlorid und derivatisiert durch Behandlung mit bis zu 3% Octenylbernsteinsäureanhydrid oder mit bis zu 2% Propylenoxid.

7. Produkt nach Anspruch 4, dadurch gekennzeichnet, daß das Kaseinat eine Mischung aus 70% Natriumkaseinat und 30% Calciumkaseinat oder aus 30% Natriumkaseinat und 70% Calciumkaseinat ist, 20 wovon 25 bis 50% durch Stärke ersetzt worden sind, und dadurch gekennzeichnet, daß die Stärke eine Wasserfluidität von 20 bis 80 aufweisende Mais-, Kartoffel- oder Tapiokastärke oder ein Derivat davon ist, hergestellt durch Behandlung mit 1 bis 3% Octenylbernsteinsäureanhydrid, 0,25 bis 2% Propylenoxid oder mit einer ausreichenden Menge an Essigsäureanhydrid, um 0,13 bis 1,6% gebundenes Acetyl zu schaffen, oder eine Wasserfluidität von 40 bis 80 aufweisende Kartoffelstärke ist, hergestellt durch Behandlung 25 mit 0,5 bis 1,5% an aktivem Chlor, wodurch das Stärke-Kaseinat-Käseprodukt dem auf Kaseinat beruhenden mozarellakäseähnlichen Produkt funktionell gleichwertig ist.

8. Produkt nach Anspruch 7, dadurch gekennzeichnet, daß die Stärke eine Wasserfluidität von 40 bis 60 aufweisendes Maisstärkederivat ist, hergestellt durch Behandlung mit 1 bis 3% Octenylbernsteinsäureanhydrid, oder eine Wasserfluidität von 40 bis 80 aufweisende Kartoffelstärke ist, hergestellt 30 durch Behandlung mit etwa 0,5 bis 1,5% an aktivem Chlor, oder ein Wasserfluidität von 60 bis 70 aufweisendes vernetztes Maisstärkederivat ist, hergestellt durch Behandlung mit bis zu 0,05% Phosphoroxychlorid und bis zu 1,5% Octenylbernsteinsäureanhydrid, wodurch das Stärke-Kaseinat-Käseprodukt im Hinblick auf den Schnitt, die Schmelzbarkeit und die Zähigkeit dem auf Kaseinat beruhenden mozarellakäseähnlichen Produkt im wesentlichen gleichwertig ist.

9. Produkt nach Anspruch 7, dadurch gekennzeichnet, daß die Kaseinatmischung 30% Natriumkaseinat und 70% Calciumkaseinat aufweist und dadurch gekennzeichnet, daß die Stärke eine Wasserfluidität 35 von 35 bis 50 aufweisendes Maisstärkederivat ist, hergestellt durch Behandlung mit 1 bis 2% Octenylbernsteinsäureanhydrid, oder ein Wasserfluidität von 65 bis 70 aufweisendes vernetztes Maisstärkederivat ist, hergestellt durch Behandlung mit bis zu 0,01% Phosphoroxychlorid und 1 bis 2% 40 Octenylbernsteinsäureanhydrid, wodurch das Stärke-Kaseinat-Käseprodukt im Hinblick auf den Schnitt, die Schmelzbarkeit und die Zähigkeit dem auf Kaseinat beruhenden mozarellakäseähnlichen Produkt gleichwertig ist.

10. Verfahren zur Herstellung des käseähnlichen Produktes nach Anspruch 1 aus Wasser, einem geschmolzenen Pflanzenfett oder einem Pflanzenöl, einem genießbaren Kaseinat, Käseadditiven und der 45 genießbaren modifizierten Stärke, dadurch gekennzeichnet, daß das Wasser und das geschmolzene Fett oder Öl durch die Kaseinat-Stärke-Mischung geliert und emulsions-stabilisiert werden.

#### Revendications

50 1. Imitation de fromage contenant au moins un caséinate comestible, caractérisé en ce que jusqu'à 80% en poids du caséinate est remplacé par un amidon modifié comestible, l'amidon étant un amidon transformé prégélatinisé ayant une fluidité à l'eau (WF) de 5 à 90, et une teneur en amylose d'au moins 15% et inférieure à 40% en poids, ou ses dérivés préparés par traitement avec jusqu'à 10% d'oxyde de propylène, jusqu'à 2% d'anhydride succinique, ou jusqu'à environ 3% d'anhydride octénylsuccinique, ou 55 avec une quantité suffisante d'anhydride acétique pour procurer un maximum d'environ 2,5% d'acétyle lié, ou avec une quantité suffisante d'orthophosphate de sodium ou de potassium, de tripolyphosphate de sodium ou de potassium, ou de leurs mélanges pour procurer un maximum d'environ 0,4% de phosphates liés, ou les produits modérément réticulés de cet amidon préparés par traitement avec l'oxychlorure de phosphore, l'épichlorohydrine, le trimétaphosphate de sodium ou l'anhydride adipique-acétique, ou les 60 amidons modérément réticulés dérivés; l'amidon transformé étant un amidon fluide préparé par traitement avec un acide ou un enzyme, ou un amidon oxydé préparé par traitement avec jusqu'à environ 2% de chlore actif, les pourcentages de traitement étant en poids sur la base de l'amidon, d'où il résulte que le substitut de fromage à base de caséinates et d'amidon est fonctionnellement équivalent au substitut de 65 fromage à base de caséinates.

2. Produit selon la revendication 1, caractérisé en ce que le caséinate est le caséinate de sodium, de

potassium ou de calcium ou leurs mélanges, et en ce que l'amidon pré-gélatinisé est un amidon séché au tambour, cuit au jet ou cuit au jet et séché par pulvérisation, l'amidon étant un amidon de maïs, de pomme de terre ou de tapioca ou leurs mélanges avec un amidon cireux, les mélanges d'amidon ayant une teneur totale en amylose d'environ 15% ou plus.

5 3. Produit selon la revendication 2, caractérisé en ce que l'amidon a une teneur en amylose d'environ 20 à 30% et est un amidon de maïs, de pomme de terre ou de tapioca à 20—80 WF, ou un dérivé de cet amidon préparé par traitement avec 1 à 3% d'anhydride octénylsuccinique, 0,25 à 2% d'oxyde de propylène, ou avec une quantité suffisante d'anhydride acétique pour procurer 0,13 à 1,6% d'acétyle lié, ou est un amidon de pomme de terre à 40—80 WF préparé par traitement avec 0,5 à 1% de chlore actif.

10 4. Produit selon la revendication 1, caractérisé en ce que le caséinate est un mélange de caséinates de sodium et de calcium dont 25 à 75% sont remplacés par l'amidon, d'où il résulte que le substitut de fromage à base d'amidon et de caséinates est fonctionnellement équivalent aux substituts à base de caséinates, de mozzarella, de cheddar ou de fromage américain fondu.

5 5. Produit selon la revendication 4, caractérisé en ce que le rapport du caséinate de sodium au caséinate de calcium est compris entre 30:70 et 70:30, en ce que le caséinate est remplacé par 25 à 50% d'amidon, et en ce que l'amidon est un amidon de maïs, de pomme de terre ou de tapioca séché au tambour, cuit au jet, ou cuit au jet et séché par pulvérisation, ou leurs mélanges avec un amidon cireux, les mélanges d'amidon ayant une teneur totale en amylose d'au moins 15% ou plus.

20 6. Produit selon la revendication 5, caractérisé en ce que l'amidon est un amidon de maïs, de pomme de terre ou de tapioca à 20 à 80 WF ou un dérivé préparé par traitement avec 1 à 3% d'anhydride octénylsuccinique, 0,25 à 2% d'oxyde de propylène, ou une quantité suffisante d'anhydride acétique pour procurer 0,13 à 1,6% d'acétyle lié, ou est un amidon de pomme de terre à 40—80 WF préparé par traitement avec 0,5 à 1,5% de chlore actif, ou est un amidon de maïs, de pomme de terre ou de tapioca à 20—80 WF réticulé avec jusqu'à 0,06% d'oxychlorure de phosphore et dérivé par traitement avec jusqu'à 3%

25 d'anhydride octénylsuccinique ou jusqu'à 2% d'oxyde de propylène.  
7. Produit selon la revendication 4, caractérisé en ce que le caséinate est un mélange de 70% de caséinate de sodium et de 30% de caséinate de calcium, ou de 30% de caséinate de sodium et de 70% de caséinate de calcium, dont 25 à 50% sont remplacés par l'amidon, et en ce que l'amidon est un amidon de maïs, de pomme de terre ou de tapioca à 20—80 WF ou un dérivé préparé par traitement avec 1 à 3%

30 d'anhydride octénylsuccinique, 0,25 à 2% d'oxyde de propylène ou avec une quantité suffisante d'anhydride acétique pour procurer 0,13 à 1,6% d'acétyle lié, ou est un amidon de pomme de terre à 40—80 WF préparé par traitement avec 0,5 à 1,5% de chlore actif, d'où il résulte que le substitut de fromage à base de caséinates et d'amidon est fonctionnellement équivalent à l'imitation de mozzarella à base de caséinates.  
35 8. Produit selon la revendication 7, caractérisé en ce que l'amidon est un dérivé d'amidon de maïs à 40—80 WF préparé par traitement avec 1 à 3% d'anhydride octénylsuccinique, ou est un amidon de pomme de terre à 40—80 WF préparé par traitement avec environ 0,5 à 1,5% de chlore actif, ou est un dérivé d'amidon de maïs réticulé à 60—70 WF préparé par traitement avec jusqu'à 0,05% d'oxychlorure de phosphore et jusqu'à 1,5% d'anhydride octénylsuccinique, d'où il résulte que le substitut de fromage à

40 base de caséinates et d'amidon est pratiquement équivalent, en ce qui concerne les caractéristiques de râpage, de fusion et l'aptitude à filer à l'imitation de mozzarella à base de caséinates.  
9. Produit selon la revendication 7, caractérisé en ce que le mélange de caséinates contient 30% de caséinate de sodium et 70% de caséinate de calcium et en ce que l'amidon est un dérivé d'amidon de maïs à 35—50 WF préparé par traitement avec 1 à 2% d'anhydride octénylsuccinique, ou est un dérivé d'amidon

45 de maïs réticulé à 65—70 WF préparé par traitement avec jusqu'à 0,01% d'oxychlorure de phosphore et 1 à 2% d'anhydride octénylsuccinique, d'où il résulte que le substitut de fromage à base d'amidon et de caséinates est équivalent en propriétés de râpage et de fusion et en aptitude à filer à l'imitation de mozzarella à base de caséinates.  
10. Procédé pour préparer des imitations de fromage selon la revendication 1, à partir d'eau, d'une

50 graisse végétale fondue ou d'une huile végétale, d'un caséinate comestible, d'additifs de fromage et d'amidons modifiés comestibles, caractérisé en ce que l'eau et la graisse fondue ou l'huile sont gélifiées et stabilisées en émulsion par le mélange de caséinates et d'amidon.

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